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CONDENSED-MATTER SPECTROSCOPY

Optical Spectroscopy and Electronic Structure of Compounds $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$)

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Abstract—The optical properties of the compounds $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) have been investigated using the ellipsometric method in the wavelength range from 0.22 to 16 μm. The electronic structure of these intermetallic compounds has been calculated in the local electron-spin density approximation with the correction for strong electronic interactions in the 4*f* shell of the holmium ions. The experimental dispersion dependences of optical conductivity in the region of interband light absorption have been interpreted based on the results of the calculation of the electron density of states. The plasma and relaxation frequencies of electrons have been determined.

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1. INTRODUCTION

The interest expressed by researchers in the intermetallic compounds RNi_5 (R is a rare-earth metal) has been associated with a wide variety of their physical and chemical properties, as well as with the prospects for their use in practice [1–3]. It is known that the electronic and magnetic characteristics of these systems undergo significant changes when nickel atoms are substituted by other *d* or *p* metals due to changes in the parameters of the electronic structure, the exchange interaction, and the crystal field. For example, a number of pseudobinary isostructural compounds $RNi_{5-x}(Cu,Al)_x$ are characterized by nonmonotonic concentration dependences of the electronic heat capacity, electrical resistivity, magnetic susceptibility, magnetic-ordering temperature, etc. [4–7]. Furthermore, doping of compounds is the main factor that favors for the improvement of the electrochemical characteristics, which affect the ability of these intermetallic compounds to absorb atomic hydrogen [8, 9]. In a number of papers [10–12], it has been suggested that there is a direct correlation between the anomalous behavior of various physical parameters of these compounds and the modification of their electronic structure with an increase in the concentration of substitutional atoms. In particular, doping of compounds leads to a change in the number of electrons in the conduction band, as well as in the electron density of states near the Fermi level E_F, which, in turn, leads to the evolution of the magnetic properties of the 3*d* subsystem.

It has been found that, in $HoNi_{5-x}Al_x$ ($x \le 2$) alloys with a hexagonal crystal structure of the parent binary compound, the electronic, magnetic, and crystalline characteristics can be significantly modified with variations in aluminum concentration x [13, 14]. An increase in the concentration of substitutional atoms leads to a decrease in the spontaneous magnetic moment, the magnetic susceptibility, and Curie temperature T_C. Moreover, the doping of the $HoNi_5$ binary compound with aluminum atoms exerts a substantial influence on the absorption properties. In particular, the unit cell of this compound at $x \sim 0.5$–1.0 can contain up to four hydrogen atoms [14].

Additional information on the specific features of the influence of the substitution of aluminum atoms for nickel atoms on the electronic structure of the aforementioned compounds can be provided by investigations of their energy spectra and spectral properties. In this work, the electronic properties of the $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) compounds have been investigated using the LSDA + U calculations of the energy-band spectrum and measurements of the frequency dependences of the optical constants. The main structural features of the dispersion curves of the interband optical conductivity have been interpreted based on the calculated electron density of states. The calculations and experiments performed have made it possible to quantitatively determine the basic parameters of the energy-band spectrum of the studied compounds at a distance of a few electron-volts from the Fermi level and their transformation with variations in the concentration of substitutional atoms.

2. CALCULATION OF ELECTRON DENSITY OF STATES

The compounds $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) crystallize in a hexagonal structure of the $CaCu_5$ type (space group $P6/mmm$) with six atoms in the unit cell and two types of nickel atoms located in the symmetrically nonequivalent positions Ni1 (2*c*) (1/3, 2/3, 0) and Ni2 (3*g*) (1/2, 0, 1 /2). The holmium atoms are located in the crystallographic positions (1*a*) (0, 0, 0). Parameters *a* and *c* of the hexagonal lattice increase with increasing aluminum concentration and have the following values: $a = 4.873$ Å and $c = 3.963$ Å for $HoNi_5$, $a = 4.923$ Å and $c = 4.035$ Å for $HoNi_4Al$, and $a = 5.025$ Å and $c = 4.076$ Å for $HoNi_3Al_2$. The self-consistent calculations of the electronic-band structure of these compounds were carried out in the local electron-density approximation taking into account strong interactions between the 4*f* electrons of the holmium atoms (the LSDA + U method) [15]. The parameters of the direct Coulomb and exchange interactions for the Ho 4*f* shell are as follows: $U = 6.5$ eV (according to experimental estimates [16]) and $J = 0.7$ eV [17]. The calculations were performed with the TB-LMTO ASA software package [18] on the basis of the tight-binding linear muffin-tin orbital atomic-sphere approximation method using the *k*-point grid in reciprocal space with the total number of *k*-points $12 \times 12 \times 12 = 1728$. The orbital basis set included muffin-tin orbitals corresponding to the 6*s*, 6*p*, 5*d*, and 4*f* states of the holmium atoms and the 4*s*, 4*p*, and 3*d* states of the nickel atoms. The Ho atomic-sphere radius was equal to 3.44 au and the atomic-sphere radii of Ni1 (2*c*) and Ni2 (3*g*) were equal 2.64 au. In these calculations, we simulated the ferromagnetic ordering of local magnetic moments on all the lattice sites under consideration. For each value of $x = 1$ and 2, all the possible configurations of the substitution of aluminum atoms for nickel atoms in the unit cell were considered and averaged over the self-consistent electron densities of states. For all the studied compounds, the obtained values of the magnetic moments on the holmium ions were close to 4.1 μ_B, whereas the magnetic moments on the nickel ions were less than 0.2 μ_B.

Total electron densities of states $N(E)$ of the $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) compounds, calculated for two opposite spin directions (↑) and (↓), are shown in Fig. 1. This figure also shows the distributions of the partial densities of the 4*f* and 5*d* states of the holmium atoms. It is characteristic that, for all three compounds, the range of high electron densities of states $N(E)$ formed predominantly by the Ni 3*d* states is located in the filled part of the valence band at energies 0–4.5 eV below E_F. The intense narrow peaks located near −8 eV in the ↑ system of electronic bands are assigned to the $4f_\uparrow$ electrons of the holmium atoms. Similar intense peaks attributed to the $4f_\downarrow$ electrons are observed within the ranges 5–6 eV below and 0.7–1.7 eV above the Fermi level. The multipeak structures of the densities of states associated with the 3*d* electrons of the nickel atoms are almost identical for the two spin directions. As the concentration of aluminum-impurity atoms increases, the intensity and energy range of this structure change only slightly. In this case, the spectral profile of electron density of states $N(E)$ undergoes a transformation, i.e., in the density of states of the $HoNi_5$ binary compound, the minimum between two groups of peaks at ~2 eV is significantly more pronounced than that of the ternary alloys. Moreover, attention is drawn to the different locations of E_F in the electron densities of states of the studied compounds. In contrast to the $HoNi_5$ binary alloy, where the Fermi level lies in the range of the density-of-states maxima formed by the 3*d* states of the nickel atoms, in the ternary intermetallic compounds the E_F lies in the range of the broad density-of-states minimum. In all the compounds, the structural features of electron density of states $N(E)$ above E_F, which are not related to the 4*f* states, have a weak intensity and are formed by a superposition of the contributions from the Ni 3*d* and Ho 5*d* bands. The calculation has also demonstrated that the contribution from the Al 3*p* band to the total electron density of states is relatively small, has a structureless form, and is almost uniformly distributed over the entire energy region shown in the figure.

3. RESULTS AND DISCUSSION

The method used for preparation of the samples and their characterization were described in detail in [4]. The spectral properties of the compounds were investigated at room temperature in the wavelength range $\lambda = 0.22$–16 μm (0.073–5.640 eV). The optical constants, such as refractive index $n(\lambda)$ and absorption coefficient $k(\lambda)$, were measured by the ellipsometric method using a rotating analyzer at angles of incidence in the range of 70°–80° with an error of 2–4%. The reflective surfaces of the samples were prepared by mechanical polishing with diamond pastes and corresponded to the 14 finish class. Using the obtained values of optical constants *n* and *k*, we calculated optical conductivity $\sigma(\omega) = nk\omega/2\pi$ (ω is the frequency of light), which is the most sensitive spectral parameter characterizing the intensity and the frequency dependence of the optical response of the reflecting medium.

The experimental optical conductivity spectra of the $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) compounds are shown in Fig. 2 (the curves are shifted upward along the ordinate axis relative to each other by 10 units). The frequency dispersion of these characteristics, in general, is typical of metal-like media and is determined by two types of light absorption, namely, intraband absorption and interband absorption. In the low-energy range $E <$ ~0.5 eV, the observed sharp increase in optical con-

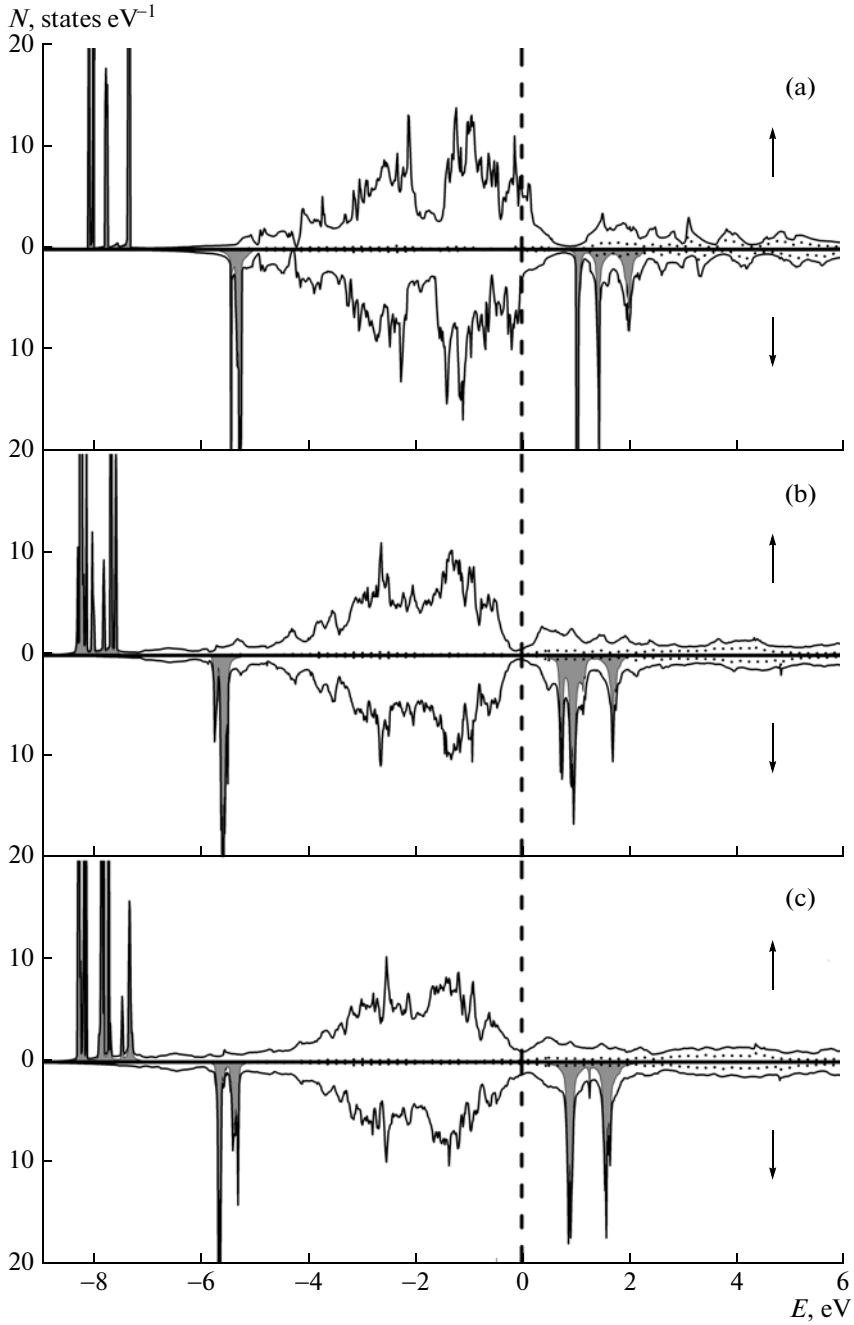

Fig. 1. Total electron densities of states (solid curves), partial densities of Ho 4*f* states (dark regions), and partial densities of Ho 5*d* states (dashed curve) of the compounds (a) $HoNi_5$, (b) $HoNi_4Al$, and (c) $HoNi_3Al_2$. The Fermi level corresponds to zero on the energy scale.

ductivity σ(ω) is associated with the Drude mechanism of the interaction of conduction electrons with an electromagnetic wave ($\sigma \sim \omega^{-2}$). With an increase in the light frequency, dependence σ(ω) exhibits a nonmonotonic behavior. This indicates that the interband transitions play a dominant role in the process of electron excitation. The optical-conductivity spectra of the three alloys under investigation in this energy range are characterized by an intense quantum absorption band, whose shape substantially depends on the impurity concentration. If the structure of the corresponding curve of the $HoNi_5$ binary alloy has a pronounced double-peak shape (maxima at 1.2 and 2.1 eV), the substitution of aluminum atoms for nickel atoms leads to the fact that the intensity of the first peak initially decreases significantly ($x = 1$), and then

($x = 2$) this peak becomes indistinguishable against the background of the low-energy side of the absorption band. In this case, the location and intensity of the second peak in the spectrum $\sigma(\omega)$ remain almost unchanged.

The changes observed in the spectral profile of dependences $\sigma(\omega)$ in Fig. 2 with an increase in the concentration of aluminum impurity atoms are caused by the transformation of the electronic structure of the studied compounds within the range of a few electronvolts from the E_F. Therefore, it was interesting to compare the experimental curves of interband optical conductivity $\sigma_{interband}(\omega)$ with the corresponding characteristics calculated from the electron densities of states (Fig. 1). Theoretical dependences $\sigma_{interband}(\omega)$ were determined using the method described in [19] and expressed in terms of the integral functions based on the convolution of electron densities of states $N(E)$ above and below E_F under the conditions of equal probabilities of the direct and indirect electronic transitions. The contributions from the $\uparrow$ and $\downarrow$ subbands to the optical conductivity proved to be additive and comparable in magnitude. The results of these calculations are presented in Fig. 3 in arbitrary units. This figure also shows interband optical conductivities $\sigma_{interband}(\omega) = \sigma(\omega) - \sigma_D(\omega)$ for the compounds $HoNi_5$, $HoNi_4Al$, and $HoNi_3Al_2$, which were obtained by subtracting Drude contributions $\sigma_D(\omega)$ from the experimental spectra. The comparison has demonstrated that, for all three alloys, the dispersion of theoretical curves $\sigma_{interband}(\omega)$ reproduces the main features of the corresponding dependences observed in the experimental spectra. The calculations have also demonstrated that the character of the transformation of spectra $\sigma_{interband}(\omega)$ due to the increase in the concentration of substitutional atoms is consistent with the tendency observed in the experiment. Moreover, it should be noted that, because of the qualitative character of the performed calculations, which disregarded the probability of the interband transitions and the lifetime of the excited state, there is no complete coincidence in details of the fine structures of the experimental and theoretical curves of the optical conductivity. For example, a large number of narrow peaks in the calculated curve $\sigma_{interband}(\omega)$ of the $HoNi_5$ binary alloy have not found confirmation in the experiment and the low-energy maxima observed in the spectra of the ternary compounds at ~0.3 eV have also not been observed in the corresponding theoretical dependences.

In general, the experiments and calculations performed have demonstrated that the structure of the dispersion curves of the interband optical conductivity of the studied compounds can be significantly modified, depending on the concentration of impurity atoms. For the ternary compounds containing aluminum, the calculated spectral profile of the absorption band is smoother than that for the $HoNi_5$ binary compound. The latter compound is characterized by an interband conductivity spectrum that consists of two broad maxima and has a clearly pronounced fine structure. According to the calculated electron densities of states $N(E)$ (Fig. 1), the nature of the formation of this band in all three alloys is associated with the electronic transitions between the Ni 3*d* bands located below E_F and the hybridized Ni 3*d* and Ho 4*f* bands above E_F. Since the electron densities of Al 3*p* states are relatively low and rather uniformly distributed over the entire energy region under investigation, no structural features associated with these states are revealed in the interband optical conductivity spectra. This character of the distribution of the Al impurity bands in the optical spectra of the studied alloys radically differs from that observed in isostructural intermetallic compounds of the $RNi_{5-x}Cu_x$ family [17, 20]. The experimental frequency dependences of optical conductivity $\sigma(\omega)$ of these compounds upon the substitution of copper atoms for nickel atoms exhibit a new intense band of quantum light absorption in the range from 3.5 to 5.0 eV due to the interband transitions of electrons from the filled Cu 3*d* band to the free Ni 3*d* band.

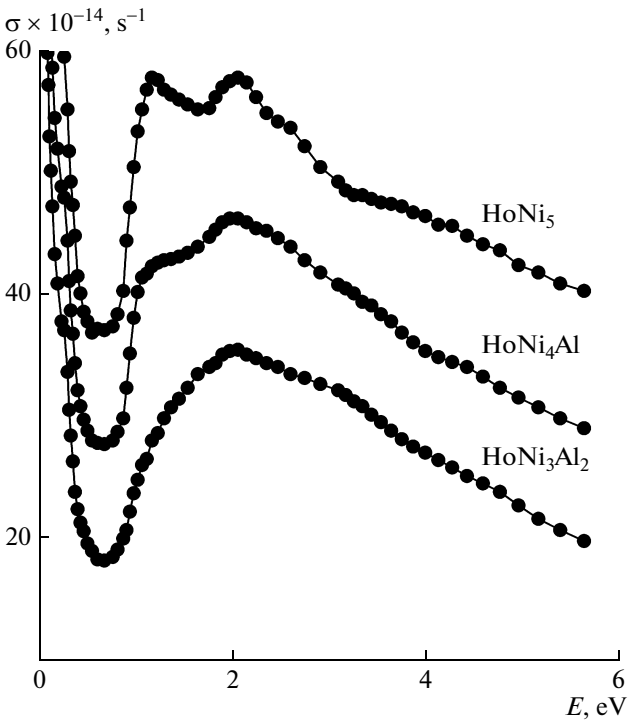

Fig. 2. Experimental dispersion dependences of the optical conductivity of the $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) compounds. The curves are shifted upward along the ordinate axis relative to each other by 10 units.

The numerical values of optical constants n and k measured in the long-wavelength (Drude) range from 10 to 16 μm, where the quantum absorption exerts a minimum effect on the optical characteristics, allow

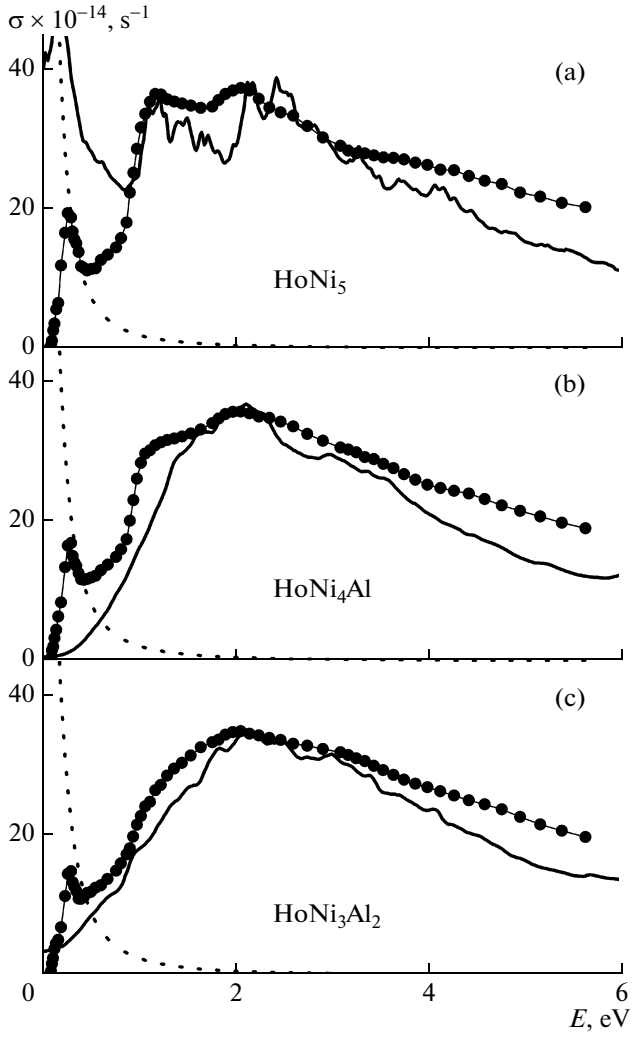

Fig. 3. Interband optical conductivities of the compounds (a) $HoNi_5$, (b) $HoNi_4Al$, and (c) $HoNi_3Al_2$. Circles are the experimental data, and solid curves represent the results of the calculation from the corresponding densities of states. The dashed lines indicate the Drude contribution calculated from the values of the parameters γ and ω_p^2.

us to determine both relaxation frequencies γ and plasma frequencies ω_p of the conduction electrons. It has been found that relaxation frequency $\gamma = 2\pi/\tau$ (τ is the relaxation time), which additively takes into account all types of scattering of electrons upon their excitation by a light wave, increases significantly with increasing concentration of Al impurity atoms and takes on the values of 1.5×10^{14} s^{-1} for $HoNi_5$, 1.9×10^{14} s^{-1} for $HoNi_4Al$, and 2.5×10^{14} s^{-1} for $HoNi_3Al_2$. The observed tendency toward a change in the square of plasma frequency ω_p^2 (the parameter determined by the specific features of the electronic spectrum in the near-Fermi region and by the electron–electron correlation effects [21]) has an opposite character: 38.7×10^{30} s^{-2} for $HoNi_5$, 35.1×10^{30} s^{-2} for $HoNi_4Al$, and 33.1×10^{30} s^{-2} for $HoNi_3Al_2$. Using the numerical values of the parameters γ and ω_p^2, we calculated the Drude contribution to the optical conductivity, which is shown by the dashed lines in Fig. 3.

4. CONCLUSIONS

The electronic structure and optical properties of the $HoNi_{5-x}Al_x$ ($x = 0, 1, 2$) compounds have been investigated. The main features of the transformation of optical conductivity spectra due to the substitution of aluminum atoms for nickel atoms in these compounds have been determined. The energy dependences of the electron densities of states calculated using the self-consistent LSDA + U method with the inclusion of strong correlations between the 4*f* electrons of the holmium atoms have been presented. The nature of electronic states that are responsible for individual features of quantum light absorption in the intermetallic compounds under investigation in the energy range up to 6 eV has been identified. The interband optical conductivities have been determined based on the calculated electron densities of states, and their behavior has been compared with the experiment. It has been shown that the character of the frequency dispersion of experimental dependences $\sigma_{\text{interband}}(\omega)$ in the region of the fundamental absorption band is adequately described in the framework of the performed calculation of electron densities of states $N(E)$. The main structural features of the quantum optical absorption revealed in the experimental curves have been identified with the additive contribution of the electronic transitions in the systems of Ni $3d_\uparrow$ and Ni $3d_\downarrow$ bands, as well as with the electronic transitions between the Ni 3*d* and Ho 4*f* bands in the $\downarrow$ system of electronic bands. The plasma and relaxation frequencies of conduction electrons have been determined from the optical constants measured in the region of intraband light absorption.

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